PYROLYSIS OF BOVINE WASTE IN A FLUIDIZED BED REACTOR

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CERTIFICATE

This is to certify that the present work "PYROLYSIS OF BOVINE WASTE IN A FLUIDIZED BED REACTOR" has been carried out under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

Pyrolysis of bovine waste was investigated in a fluidized bed reactor.

Bovine waste was pulverised and separated into three fractions of -30+44, -44+72 and -72+100 mesh size. These fractions were then pyrolysed separately at various temperatures ranging from 600 to 800°C under isothermal conditions. The effect of temperature and particle size on the conversion, products yields and composition, and heating values of products was studied. The products were gas and char. No liquid product was observed. The total gas yield was found to increase with temperature and decrease with particle size. Methane and hydrogen yields decreased and carbon dioxide yield increased as the particle size was increased. The composition as well as yields of carbon monoxide and hydrogen increased with temperature, of carbon dioxide decreased with temperature and methane yield showed a maximum at 650°C. The product gases had highest heating value of 2960 KCal/cu.m. for -30+44 mesh size particles at temperature 650°C.

CHAPTER 1

INTRODUCTION

With the dwindling supply of fossil fuel, efforts are being made to find alternative sources of energy. Solid waste, which represents a huge disposal problem, and can be obtained at negative cost, is being investigated by various workers as a raw material for producing fuel[1]. The different kinds of waste being investigated are agricultural waste, bovine waste, municipal solid waste etc.

Due to the religious beliefs of its people and rural based population, India has an immense cattle population estimated at 220 million[2]. Each animal, on an average, produces 8 to 15 lbs of manure per day and the total production of bovine waste in India has been estimated as 800 million tons annually[3]. At present, it is used either as a low grade fertilizer or dried for use as fuel. (The use in gobar gas plants is still very limited). Bovine waste, as received, contains 30 to 35 % carbon and 3.5 to 7.0 % hydrogen and has heating value of 3,000 to 4,000 K-Cal/kg. Thus, bovine waste, if it can be economically converted to fuel, represents an inexhaustible supply of energy and besides reducing the environmental pollution,

can go a long way in reducing the import of fossil fuels.

A number of processes can be used to convert solid waste to fuel and to other usable chemicals although all of them may not be practically feasible. Considerable amount of work is in progress to convert it to fuel. The processes which are being investigated presently by various worker are anaerobic digestion [4], hydrogasification [5], pyrolysis [6], and partial oxidation [7].

Anaerobic digestion consists of gasification of organic wastes by methane producing bacteria in the absence of oxygen. The complex organic materials present in the waste, are first converted to alcohols, aldehydes and acids by acid forming bacteria. In the second stage these materials are converted to methane and carbon dioxide. The gas produced contains 50 to 80% methane and 20 to 50% carbon dioxide. This method has the disadvantage of being very slow and depends upon the weather conditions. The methane producing bacteria die over 40°C while the rate of digestion is very low at lower temperatures. Another problem is the agitation of the slurry. Beside this only a batch process is feasible.

Hydrogasification is a viable process but it has the disadvantage that very high hydrogen pressures (approx. 1000 psi) are required. Since hydrogen is not easily available in India, this process was not investigated.

In the partial oxidation process, steam and air (or oxygen) mixture is reacted with the solid waste. Both, pyrolysis and oxidation occur in the reactor. The endothermic heat of pyrolysis is supplied by burning the residual char with oxygen. Compared to pyrolysis, the energy requirements are lower, however the heating value of product gases is also lower.

Pyrolysis consists of thermal decomposition of an organic substance in the absence of oxygen. Pyrolysis reaction is of following type[8].

Carbonaceous Solids $\xrightarrow{\text{heat}}$ High and moderate molecular wt. organics + Char + liquids (tar and oils) + low molecular wt. organic liquids + methane, hydrogen, water, carbon monoxide, carbon dioxide + Ammonia, Hydrogen sulphide + hydrocyanic acid.

The process can be carried out at atmospheric pressure and at temperature generally above 500°C. This process has the advantage that almost any type of organic waste can be

pyrolysed, however the yield of products and its composition depends upon the feed composition. Several pyrolysis systems are being developed to convert organic fraction of solid waste to synthesis gas or oil. Snyder[9] has described four pyrolysis systems which are Union Carbide's Purox process, Andco's Torraxe Process, Monsanto's Landgard Process and Occidential's Flash Pyrolysis Process. Out of these the first produces a fuel which is either storable or transportable; Torrase and Landgard processes produce hot nitrogen rich synthesis gas which must be burned immediately for use in generating steam as the primary commodity and the main product from Flash pyrolysis is fuel oil which can be used to replace No. 6 fuel oil.

Only a few continuous fluidized bed systems for pyrolysis and gasification have been developed[10] and the process data available is very scanty. In order to design a plant processing manure to fuel, the conversion and product yields as a function of residence time, temperature and particle size would have to be known. There is no data available on the effect of particle size on the product yields in pyrolysis of waste in fluidized beds.

The aim of the present investigation was to study the effect of temperature and particle size on the conversion, yield and product distribution in fluidized bed pyrolysis.
of bovine waste.

CHAPTER 2

LITERATURE REVIEW

Manure from any type of cattle contains almost same types of compounds though their relative amount may vary. These are polysaccharides and long chain aromatic polymers which are usually found in plant cell.

According to Grub [11] main components of cattle manure are undigested food, unabsorbed digestive juices, cells and mucous from the digestive tract and the waste minerals. Cattle manure contains about 40 percent (by weight), of cellulosic materials. Other major compounds are hemicellulose and lignin. Therefore pyrolysis of these materials will give some idea about the pyrolysis of manure.

According to Grub [11] dry cellulose when heated slowly in the presence of air and moisture in various liquids, gave tar and gases at 230–240°C. The rate of production of gases were highest in the temperature range of 270 to 350°C. The gases consisted of carbon monoxide, carbondioxide, hydrogen, methane and other hydrocarbons. Tar consisted of aromatics and other heavier organic compounds.

Grover, Barbour and Freed[12] found that the main products of cellulose pyrolysis were carbon, carbon dioxide and water. Their relative amounts varied with the variation in pyrolysis conditions i.e. temperature, duration of heating, surrounding conditions and impurities.

Nikitin [13] pyrolysed wood and found that the decomposition started exothermally at about 270-280°C and yielded gases and liquid distillates and tars. The major gaseous components were carbon monoxide and carbon dioxide. When pyrolysis temperature was raised to 300-400°C gases produced contained carbon monoxide, carbon dioxide, methane and traces of other hydrocarbons.

The pyrolysis of manure was studied by Garner and Smith[14] but their object was to maximise yield of liquid organic compounds. They found that yield was maximum at low pressure and in the temperature range of 400 to 500°C. Under these conditions the non condensable gases contained 8.6 percent hydrogen, 10.9 % nitrogen, 16% CO, 38.9 CO_2, 12.9 % methane, 0.3 % ethylene and 1.8 percent ethane. The gases produced had heating value of 2-3 million BTU per ton of dry manure.

Rosin [15] and others pyrolysed solid municipal refuse and found four basic products; gases, water, organic liquid

and char. The product distribution was found to vary with changes in heating rate. The main components of gases were methane, hydrogen, carbon dioxide and carbon monooxide. Ethylene and ethane were also present in gases but were in traces. Hoffman[16] pyrolysed municipal solids refuse and found that optimum temperature of pyrolysis with the minimum pyrolysing time occurred at 815°C for materials having bulk density of around 15-20 lbs per cu.ft.

Kilburn[17] studied the pyrolysis of Wood in a fluidized bed reactor, to investigate the effect of temperature and heating rate of an yield of products, and product distribution. He found that wood pyrolysis gave a gas with a heating value of approximately 360 Btu/cu.ft. P.S. Maa and R.C. Bailie[18] carried pyrolysis of wooden cylinders in an isothermal fluidized bed reactor in the temperature ranges of 600-1200°C. They observed that pyrolysis occurred with shrinking core model and pyrolysis rate increased with the increase of fludized bed temperature.

Baila R.C. and Barton, R.S. [19], carried the pyrolysis of municipal solid waste in a fluidized bed reactor. Their studies showed that solid waste injected into hot fluidized sand bed would produce a fluel gas which was comparable

to gas generated from coal gasification system developed for converting coal into synthetic natural gas.

A According to them, as a result of high rate of heat transfer to the refuse injected to the bed, the organic molecules were thermally shattered into small gaseous fragments. Experiments had shown that the gas formed contained 60-75% of the energy originally available from solid waste. The conversion of carbon (in the refuse) to the gas was in the range of 65-85 percent.

Habibullah[20] conducted the pyrolysis of solid bovine waste in an isothermal fixed bed reactor, in the temperature range of 600-650 °C for -13+30, 30+72, -72+100 mesh size particles. He observed that composition of the product gases varied with the temperature and particle size. The molar percent of hydrogen and carbon monoxide increased with increasing temperature whereas the molar percent of methane showed a maxima at a temperature range of 450-500 °C. The heating value of the product gases was highest at 500 °C and was of the order of 3854 KCal./Cu.m. For the same temperature, gas yield increased as the particle size was reduced. The heating values of char obtained varied with temperature and feed particle

size and was higher for larger particles.

Bovine waste pyrolysis has not been done in the higher temperature range in fluidized bed reactor. Moreover the effect of particle size on yield and distribution of product for bovine waste pyrolysis has not been studied inafluidized bed.

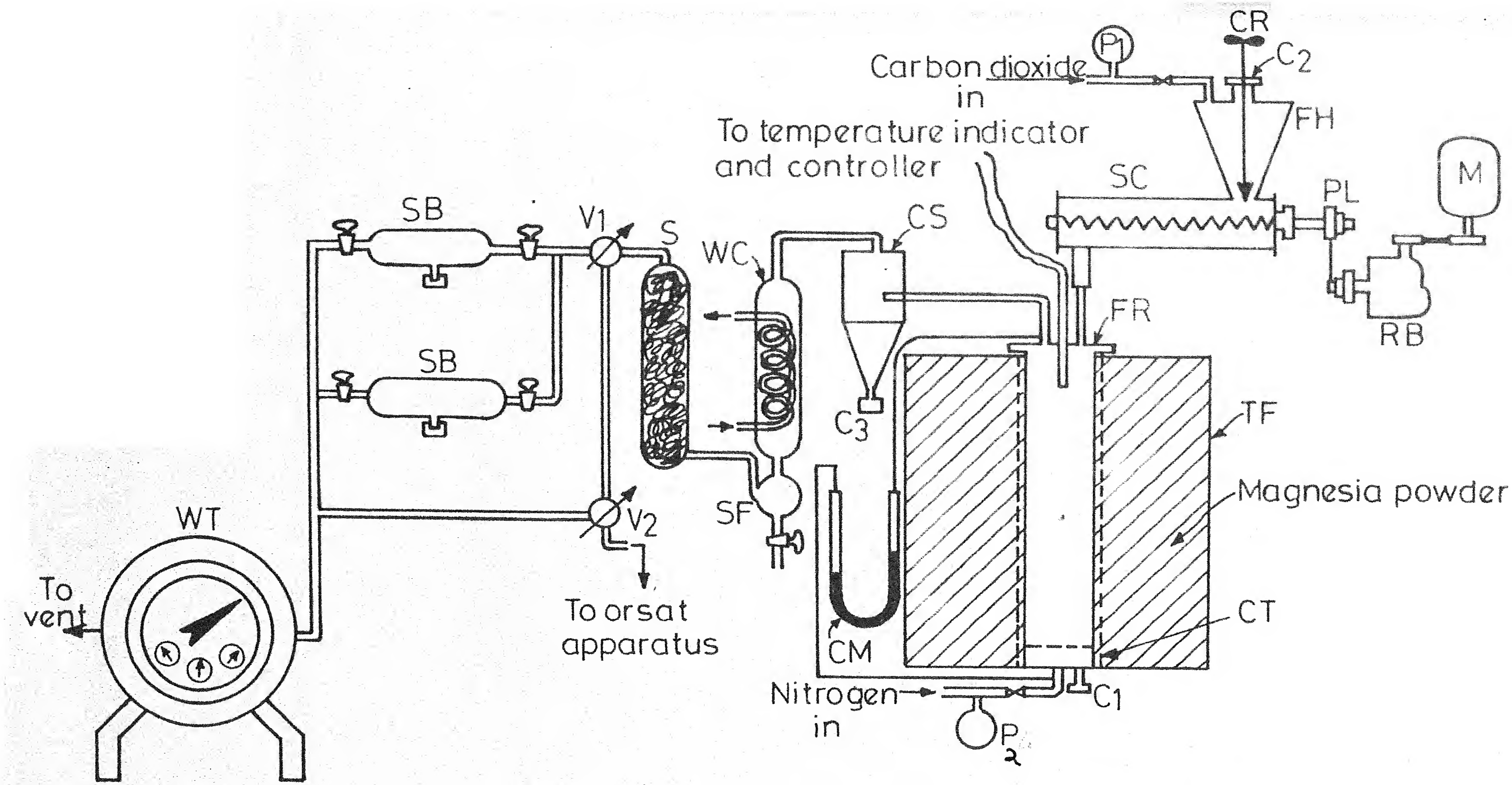
CHAPTER 3

EXPERIMENTAL SET UP AND PROCEDURE

3.1 Experimental Set up:

The pyrolysis was conducted in a continuous fluidized bed reactor and a schematic diagram of the apparatus is shown in Figure 1.

The fluidized bed reactor (FR) was constructed of 60 cm long piece of 52 mm. O.D. stainless steel pipe. Provision was made for feeding two gases simultaneously to the reactor so that the same setup could be used for further studies on partial oxidation. For this, a 12 mm O.D., 5 cm long, stainless steel tube was welded at the base of the reactor, the other end of which was connected to a 1/4 inch standard Tee-joint. In the pyrolysis study, one inlet was used for feeding nitrogen gas, the other inlet was closed permanently. The top flange of the reactor contained a feed inlet connected to the outlet of the screw conveyor (SC), a 12.5 mm O.D., 50 mm long stainless steel tube for the product gases and char outlet and a 6 mm hole in the centre for placing a thermowell in the reactor. Any material retained in the reactor was removed through a 12 mm O.D. outlet provided with a cap (C_1) and welded to the base of the reactor. To provide uniform



WT - Wet testmeter
SB - Sampling bulb
S - Scrubber
V_1,V_2-Three way valve
WC - Water cooled condenser

CS - Cyclone separator
SF - Separating funnel
TC - Thermocouple
P_1,P_2-Pressure regulator
C_1,C_2,C_3- Cap

CM - Carbon tetrachloride manometer
CT - Ceramic tube
TF - Tubular furnace
FR - Fluidized bed reactor
SC - Screw conveyor

FH - Feed hopper
CR - Clearing rod
M - Motor
RB - Reduction gear box
PL - Pulley

Fig. 1 : Experimental set-up for pyrolysis of bovine waste in fluidized bed reactor.

distribution of the fluidizing gas, the reactor contained a gas distributor plate welded 25 cm above the base. The gas distributor was made from a 1/4 inch thick stainless steel plate and it's diameter was equal to the inner diameter of the reactor. It had 8 equidistant holes of 1.6 mm diameter along a concentric circle of 35 mm diameter. To support the solid, a 200 mesh wire screen was fixed above the distributor plate. Though the design of gas distributor was available, it was preferred to carry fluidization studies over an identical glass reactor, with different types of distributors to select one giving the best fluidization and also to get an idea of fluidizing velocity.

The screw conveyor was developed for continuous uniform feeding of bovine waste at rate of 7 to 20 grams per minute. It consisted of a mild steel worm of 38 mm diameter and 45 mm length having a helically wound blade of 3mm depth at a pitch of 4cm. This worm was rotated in ball bearings which were fixed to the flanges of a 10 cm O.D. mild steel pipe. The rotation was provided with 1420 r.p.m., 0.5 hp. motor (M) and the speed reduced and varied through a 50:1 reduction gear box (RB) and various sets of pulleys (PL). The speed of the screw feeder could be varied from 14 to 45 rpm. The bovine waste was fed to

the screw feeder through a conical feed hopper (FH). Two inlets were provided at the top of the feed hopper. One provided with a cap (C_2), was used for charging the hopper and other to supply a slow stream of metered carbondioxide. This carbondioxide pressure was provided to prevent the product gases from entering the screw feeder and hopper. Preliminary runs indicated that clogging of the feed line occurre at the junction of the feed hopper and screw feeder. To eliminate this and ensure uniform feeding a leakproof arrangement was made for the reciprocatory motion of a 1/4 inch O.D. rod (CR) in the hopper. This rod was passed through the cap of the feed inlet pipe and reached till the junction. A decrease in the flow rate of the solid was marked by an abrupt decrease in the out let flow rate of the gases and the way was cleared by manipulating CR.

The reactor was placed in a 1200 Watt tubular furnace of the same height as that of the reactor. The furnace permitted operation till temperature upto 1000 °C. It was constructed of 16 gauge Kanthol heating wire with a total resistance of 20 ohms. This wire was wound over a 54 mm I.D. ceramic tube (CT). A layer of asbestos cement was applied over the heating element and the whole assembly was fixed in the centre of 46 cm diameter aluminium body.

The space between the aluminum body and ceramic tube was filled with about 60 kg. of magnesia powder. The magnesia powder provided the insulation and insured that the heat losses to the surroundings were low. As mentioned earlier, the top of the reactor contained a gas and char outlet. This was connected to a cyclone separator (CS) of 7.5 cm diamete to separate the gas from solid char. The solid product which collected in the cyclone could be removed from the bottom. The gases from the cyclone separator were passed through a water cooled condenser and any condensables were collected in a separating funnel (SF). The non condensables from the condenser (WC) were scrubbed of any fine char particles by passing through a glasswool scrubber (S) and were then sent through a sampling bulb (SB) to the wet testmeter (W T) and then vented. The sampling bulb had a sampling port in the centre which was closed with a self sealing silicon septum. Two three way valves (V_1 and V_2) were provided between the sampling bulb and the scrubber so that, when desired a gas sample could be collected for Orsat analysis. The chromel-alumel thermocouple was insulated with ceramic beads and placed in a 6 mm. O.D. 60 cm. long thermowell. This served as a sensor for the temperature controller which regulated the power to the furnace. The thermowell was coaxial with the reactor and movable

along the axis. For any run it could be adjusted at the desired height and sealed with a mixture of lead oxide and glycerine.

The nitrogen for fluidization was measured with a caliberated orificemeter. The pressure drop across the reactor was measured with a manometer filled with carbontetrachloride. For this two small lengths of 3 mm O.D. stainless steel tubing were welded at the inlet and outlet of the reactor and connected to the manometer.

3.2 Analytical Equipment:

Analysis of individual components in the product gas was performed by a combination of gas chromatorgraphy and Orsat analysis. For the analysis of hydrogen and methane gas chromatograph was used. A 6 meter long, 6.25 mm O.D.copper tubing packed with -40/100 mesh silica gel was used at 140°C. The carrier gas was nitrogen at a flow rate of 50 cc /mn . The chromatograph used for this work was a F and M laboratory gas chromatograph. It was a dual column chromatograph and was equipped with a thermal conductivity detector. A single speed Texas instrument company recorder was used to measure the response from the detector. Since the senstivity of the detector for carbom monoxide and

carbondioxide was poor, these gases, were analyzed on an Orsat apparatus. In the Orsat analysis , ammonical cuprous chloride solution was used as absorbent for carbon monoxide and forty percent potassium hydroxide solution for carbon dioxide.

3.2.1 Chromatographic Analysis:

The method used for the quantitative analysis of the gases for this study was to inject different volumes (V_i) of the same component and measuring the corresponding areas (A_i). Knowing V_i and A_i over a wide range, the slope of the plot gives f_i' , where

$$V_i = f_i' \cdot A_i$$

The same procedure was repeated for other components expected to be present in the sample. The retention times were noted by injecting pure components. Calibration curves for hydrogen and methane are given in Appendix 1.

3.2.2 Operating Conditions of Chromatograph:

Type of column : Activated silica gel

Column oven temperature: 140°C

Injection port temperature: 70°C

Detector cell temperature: 200°C.

Bridge current	:	60 mA
Type of carrier gas	:	Nitrogen
Carrier gas flow rate	:	50 c.c. per minute
Carrier gas pressure	:	2.5 kg. per square cm. (37 psi)
Sample size	:	5 ml.

3.3 Raw Materials:

The bovine waste feed was obtained from a village near by Kanpur and was dried, crushed and sieved and then -30+44, -44+72, -72+100 mesh size fractions were used as feed. These fractions were characterised for their carbon, hydrogen, nitrogen, ash and moisture content. Moisture content was determined by the weight loss upon drying over night at 105°C. The ash content of the feed was taken as the material remaining upon ignition in a muffle furnace operated at 750-800°C. The heating values of all the fractions were also determined on an adiabatic bomb calorimeter. The composition of various samples are presented in Table 1.

TABLE 1 : CHARACTERIZATION OF BOVINE WASTE SAMPLES

	Particle size, Mesh No.	-30+44	-44+72	-72 +100
1.	Moisture content percent (dry basis)	6.7	6.0	5.3
2.	Ash content (As received basis)	22.4	27.5	29.9
3.	Ultimate analysis (dry basis)			
	Carbon percent	35.9	35.2	35.2
	Hydrogen percent	3.3	3.7	4.7
	Nitrogen percent	None detected	None detected	None detected
4.	Gross heating values (As received basis) K.Cal.per kg.	3560	3289	3236

3.4 Experimental Procedure:

The pyrolyses were conducted at atmospheric pressure and at various temperatures ranging from 600-800°C. To start a run the reactor was heated to the desired temperature. The screw conveyer was loaded with a weighted amount of bovine waste. After the reactor had reached the desired temperature, a slow stream of nitrogen was passed from the base of reactor and a slow stream of carbon dioxide was passed through the top of the hopper to purge the air from the system. This flushing was continued for 30 minutes. The flow rate of nitrogen was then adjusted such that it would result in good fluidization. The fluidization characteristics of the feed had been previously determined experimentally on an identical glass apparatus. The effect of temperature and of produced gases were also taken in to account. After this, the bovine waste was fed through the screw conveyor, and the reactor allowed to reach steady state. The flow was marked by an increase in the pressure drop across the reactor. Preliminary runs had indicated that the composition and flow rate of product gases stabilized after ten minutes; therefore, the product samples were not collected for the first twenty minutes. It was only after this steady state had reached that the data were taken.

To take the data, the char which had collected in the unsteady state period was taken out from the cyclone separator For a known period of time, which was usually ten minutes, the total volume of effluent gases was measured. The off gas samples were collected and analyzed for methane, hydrogen by chromatography and carbon monoxide and carbondioxide by Orsat analysis. No measurable liquid condensate was obtained. At the end of the runs, the furnace was shut off to cool the reactor to room temperature. Then the weight of bovine waste was determined by weighing the amount remaining in the screw feeder and hopper. The weight transferred during the total run time was calculated by difference and the amount transferred in the steady state period calculated by assuming that the flow rate was constant. Performance of the screw feeder had already been checked. The solid flow rate remained constant if the load in the screw conveyor was maintained constant by occasionally tapping and cleaning the hopper. At the termination of each run, the chars from the reactor and from the cyclone separator were separately collected and weighed. The char from the cyclone separator and that from the reactor was thoroughly mixed; its ash content was determined by heating the char in a muffle furnace maintained at 750–800°C and the heating value was measured by an adiabatic bomb

calorimeter.

The same procedure was repeated for various temperatures and particle sizes. The runs were taken for one solid feed rate of nearly seven grams per minute. Lower feed rates were not possible due to the limitation of the gearbox and pulleys and with higher flow rates the reactor solid inlet line and the produce outlet tube were clogged in a short time.

CHAPTER 4

RESULTS AND DISCUSSION

Pyrolysis of bovine waste was conducted at atmospheric pressure and various temperatures to investigate the technical fessibility of transforming bovine waste to fuel gas in a fluidized bed reactor. Initially attempt was made to remove the solids from the reactor continuously but the arrangement did not work satisfactorily. In the modified arrangement the solid was fed continuously and the char was entrained by the product gases and nitrogen. Most of the char was entrained, however, a small percentage of the total char collected in the reactor. Thus, strictly speaking, the runs were not steady state runs, however only 11 to 19 percent of the total char was retained in the reactor and for practical purposes, it could be assumed that the data taken, were at the steady state.

The pyrolysis was studied for -30+44, -44+72 and -72+100 mesh size of bovine waste. For each mesh size the pyrolysis was conducted at different temperatures ranging from 600-800°C. This temperature was measured 12 cm below the top flange of the reactor. The thermowell was not

placed till the bottom of the reactor because it could have caused poor fluidization. The maximum temperature variation along the length of the reactor was 90°C. For each run, bovine waste was fed at a rate of around 7 grams per minute. After the steady state had reached, data were taken for a run time of 10 minutes. The data which were taken, measured the total amount of non condensable gases and it's composition, the total weight, heating value and ash content of char, weight of bovine waste transferred and the flow rates of nitrogen and carbon dioxide. The methane and hydrogen content in the off gases was determined by gas chromatography as discussed earlier, while carbon monoxide and carbon dioxide by Orsat analysis. By a nitrogen material balance the amount of other non identified gases was estimated. In the temperature range of 600-650°C, small amounts of liquid products were also produced but could not be measured because they adhered to the surface of the cyclone separator and condenser. The flow rate of nitrogen was kept constant at 4.08 lpm and of carbon dioxide at 0.3 lpm for all the runs. Tables 2-4 show the amount of the various input and output streams for different temperatures and particle sizes. The overall recovery varied from 93 to 98 percent. The deviation could be due to slight variations in the solid feed rate and due to the formation of tars which

could not be collected. Moreover the molecular weight of the gases for the material balance did not take into account the presence of the unidentified heavier compounds.

4.1 Effect of Temperature on Gas and Char Yield:

Figures 2,3,4 show the effect of temperature on the gas and char weight percents for -30+44, -44+72, -72+100 mesh sizes particles, respectively. For any particular size, the gas yield increases and char yield decreases with the increase in temperature. For example, for the -72+100 mesh size the gas yield increased from 58.0 to 62.0 weight percent as the temperature was increased from 600 to 800°C. This shows that even at 600°C, the pyrolysis is nearly complete. There was some doubt as to whether the residence time in the reactor was sufficient for complete pyrolysis or not. Habibulla[20] pyrolyzed the manure sample at 650°C in a fixed bed reactor and determined the percentage of gases till the evolution of gases had stopped. His results show that at 650°C, the gas yield is 63.2 percent (weight basis) compared to 59.5 percent in this study. Thus we concluded that pyrolysis in our study was nearly complete. However, slight increase in gas yields and decrease in the char yields with the increase in the temperature were due to

TABLE 2 : OVERALL MATERIAL BALANCE FOR PYROLYSIS OF BOVINE WASTE FRACTION (-30+44) MESH SIZE

Basis : 10 minutes

	TEMPERATURE °C				
	600	650	700	750	800
Input in grams					
Bovine waste	67.0	65.2	69.0	64.8	66.8
Fludizing Nitrogen	47.5	47.5	47.5	47.5	47.5
Carbon dioxide from top of feeder	5.5	5.5	5.5	5.5	5.5
Total	120.0	118.2	122.0	117.8	119.8
Output in grams					
Off Gases	92.6	92.5	95.5	93.6	94.5
Solid Char	20.1	18.2	18.9	16.2	17.2
Total	112.7	110.68	114.37	110.47	111.7
Recovery (%)	93.9	94.1	93.7	98.3	93.2

TABLE 3 : OVERALL MATERIAL BALANCE FOR BOVINE WASTE FRACTION (-44+72) MESH SIZE

Basis : 10 Minutes

	TEMPERATURE °C				
	600	650	700	750	800
Input in Grams					
Bovine Waste	69	74	74	67	69
Fluidizing Nitrogen	47.5	47.5	47.5	47.5	47.5
Carbon dioxide from top of feeder	5.5	5.5	5.5	5.5	5.5
Total	122.0	127.0	127.0	120.0	122.0
Output in Grams					
Off Gases	94.5	97.8	97.2	93.7	97.1
Solid Char	22.1	22.0	24.3	19.8	17.8
Total	116.6	119.8	121.5	113.5	114.9
Recovery (%)	95.5	97.8	95.6	94.5	94.5

TABLE 4 : OVERALL MATERIAL BALANCE FOR BOVINE WASTE FRACTION (-72+100) MESH SIZE

Basis : 10 Minutes

	TEMPERATURE °C				
	600	650	700	750	800
Input in Grams					
Bovine Waste	71.0	67.3	69.3	70.0	73.0
Fluidizing nitrogen	47.5	47.5	47.5	47.5	47.5
Carbon dioxide from top of feeder	5.5	5.5	5.5	5.5	5.5
Total	124.0	120.3	119.3	123.0	126.0
Output in Grams					
Off Gases	94.3	93.12	94.58	96.0	98.22
Solid Char	25.2	23.1	22.5	21.2	21.2
Total	119.5	116.22	117.08	117.2	119.42
Recovery (%)	96.3	96.6	95.7	95.3	97.4

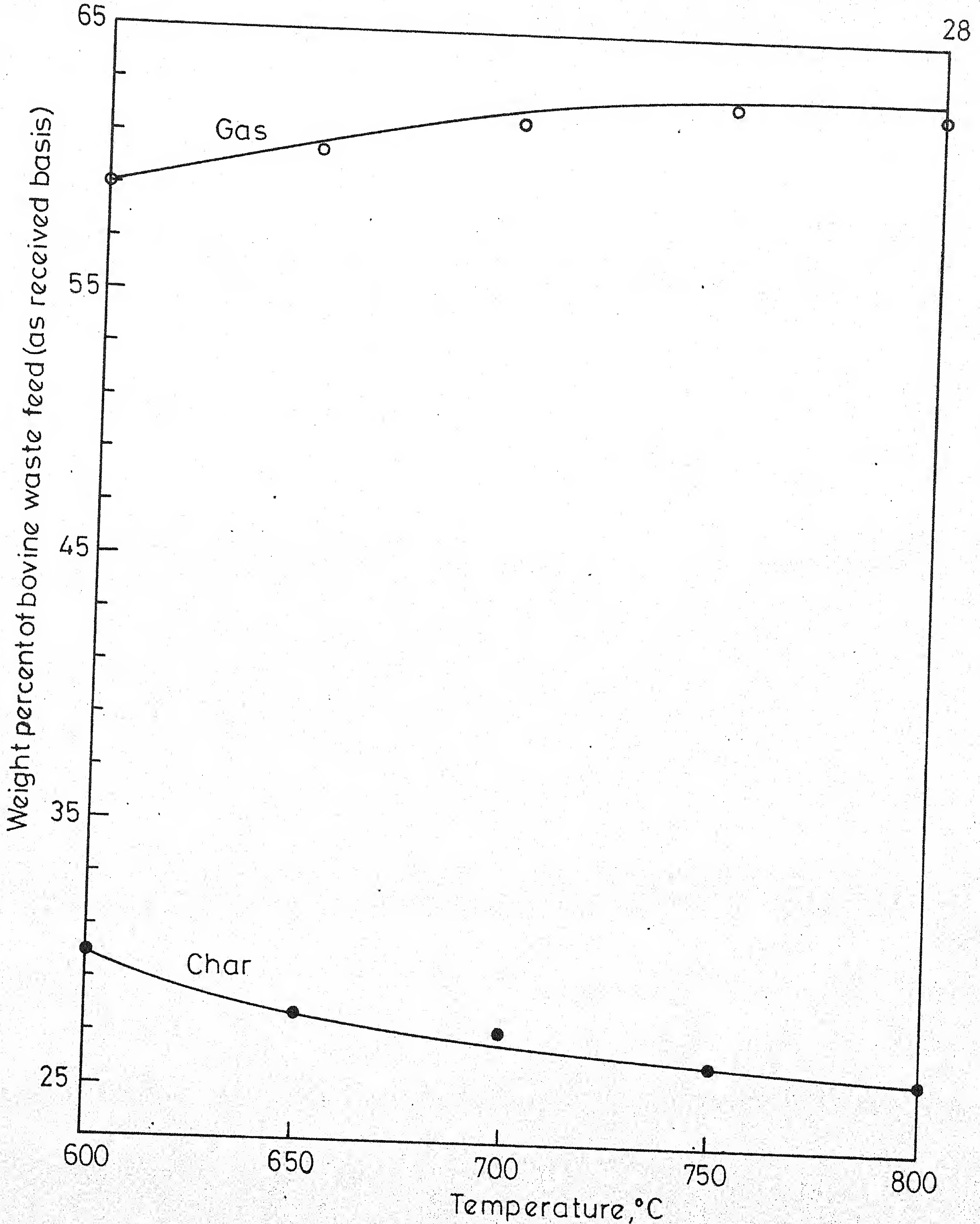


Fig. 2 : Effect of temperature on gas and char yield (fraction -30 +44).

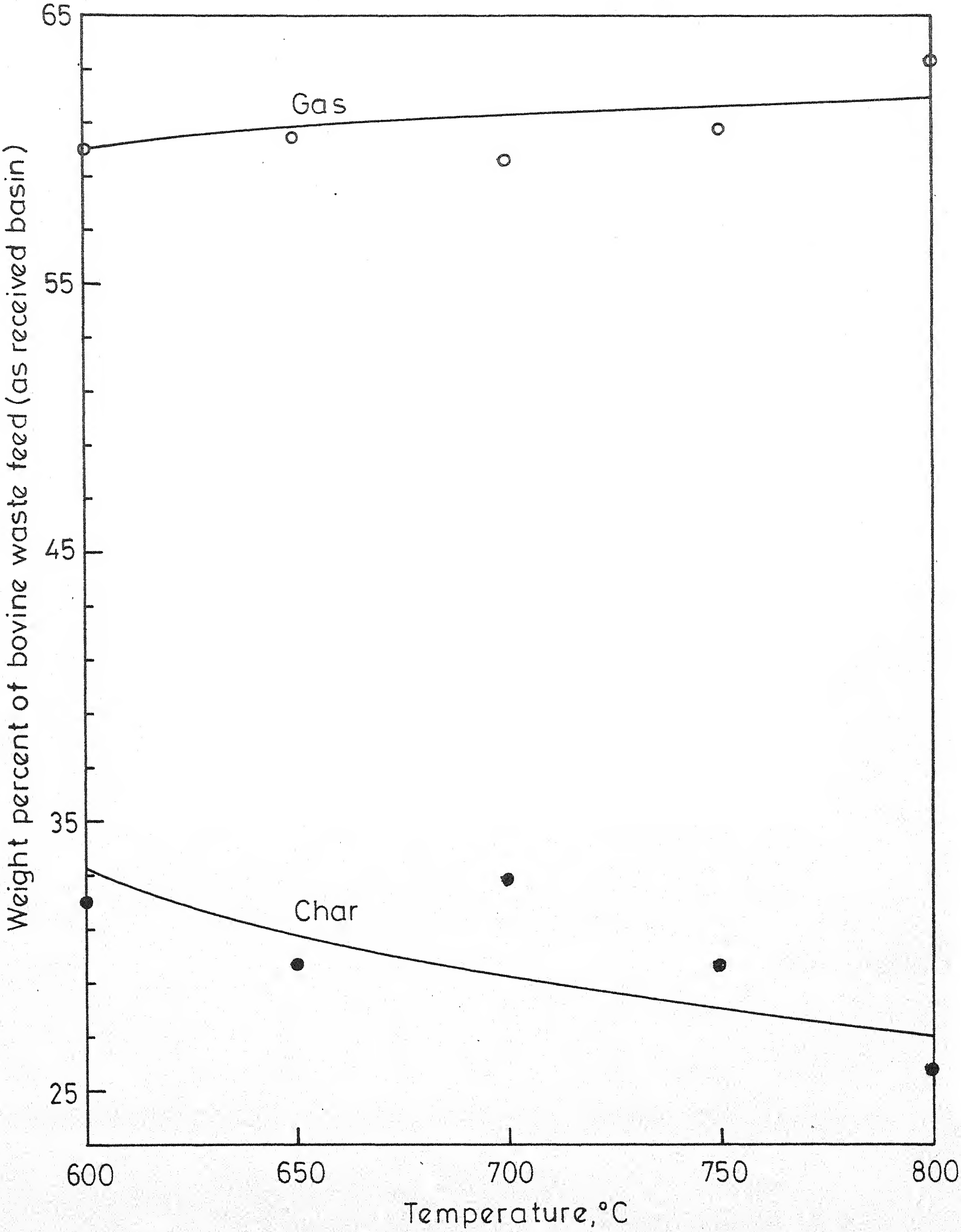


Fig. 3 : Effect of temperature on gas and char yield (fraction - 44 + 72).

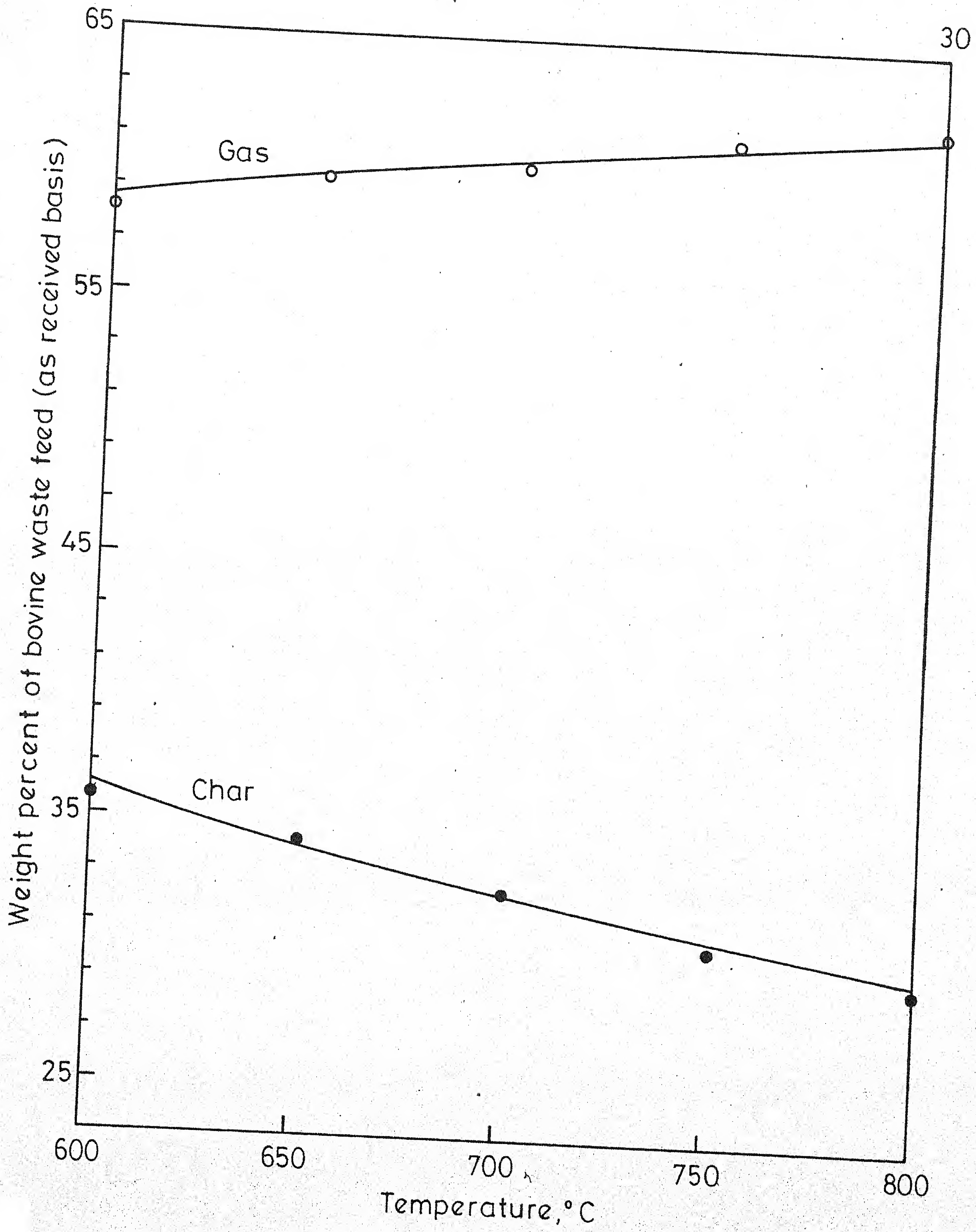


Fig. 4 : Effect of temperature on gas and char yield (fraction −72 +100).

the following secondary reactions which are faster at high temperatures.

$$C + H_2O\ (g) \longrightarrow CO + H_2 \qquad \ldots\ldots \quad (i)$$

$$C + CO_2 \longrightarrow 2CO \qquad \ldots \quad (ii)$$

Besides the reactions (i) and (ii) the other important secondary reactions which take place in pyrolysis of solid wastes are

$$CH_4 + H_2O\ (g) \longrightarrow CO + 3H_2 \qquad \ldots \quad (iii)$$

$$CO + H_2O\ (g) \longrightarrow CO_2 + H_2 \qquad \ldots \quad (iv)$$

4.2 Effect of Particle Size on Gas and Char Yield:

There was no discernible trend of gas yield weight percent (on as received basis) with particle size. However, as shown in Table 1, the ash contents for the three particle sizes were different. To compare the gas yields on a common basis, the weight of gases produced per 100 gram of ash free waste feed were calculated. This variation is shown in Fig.5. It shows that weight of gases produced increases as particle size decreases. If we assume that the shrinking core model which describes the pyrolysis of cellulosic materials [18], is also applicable to the pyrolysis of bovine waste then the variation becomes clear.

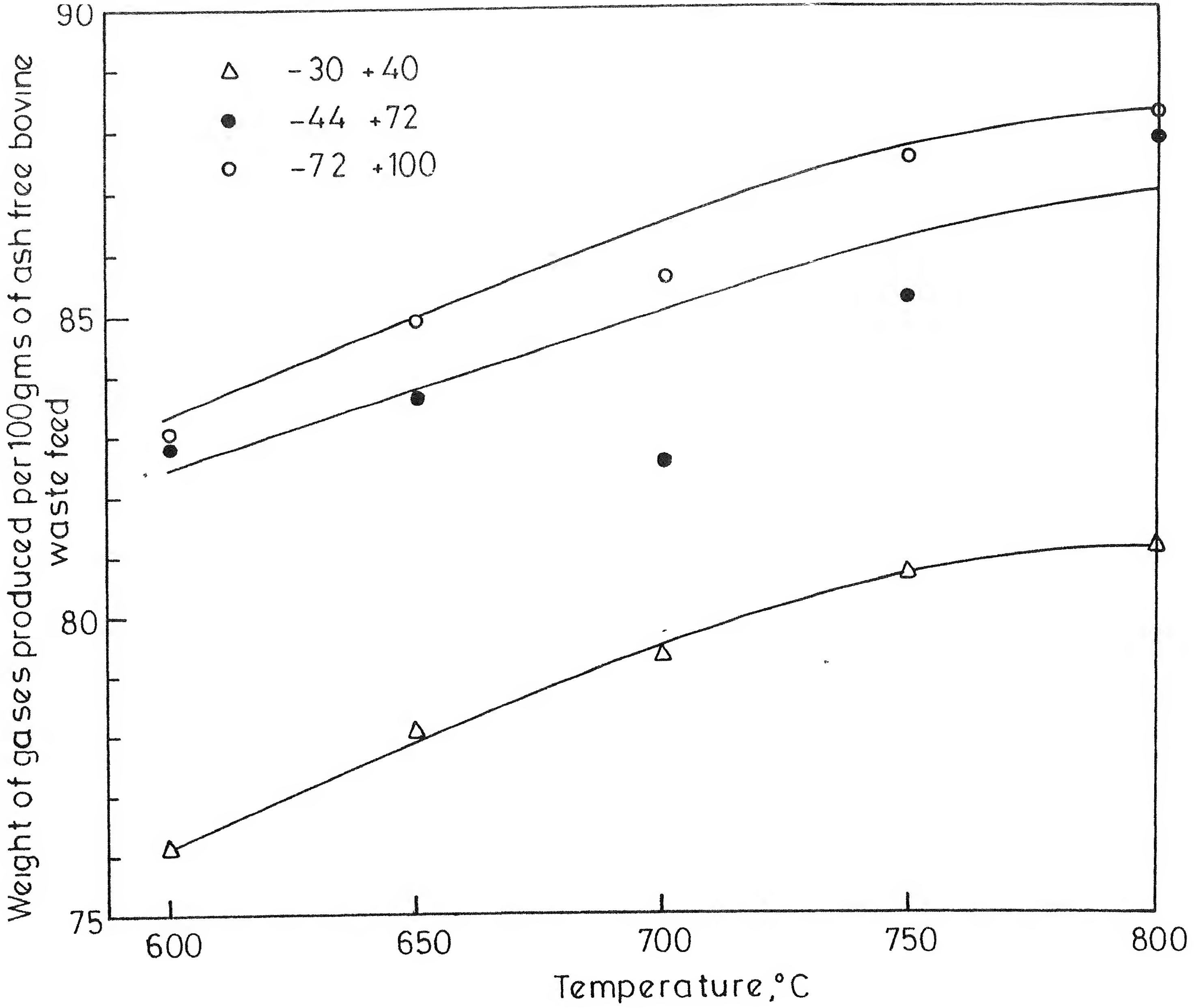


Fig 5 Effect of temperature and particle size on weight of gas produced per 100 gm ash free feed

In examining the cross-section of the partly reacted solid particles, it is usually found that there is unreacted solid material surrounded by a layer of ash. This indicates that the reaction occurs first at the outer skin of the solid particles, then the reaction zone moves in to the solid, leaving behind ash. Since the pyrolysis is an endothermic reaction, the temperature at the interior of the particles is lower than that of the reactor, and consequently the pyrolysis rate is lower.

4.3 Effect of Particle Size and Temperature on Gas Composition

Since nitrogen was used as the fluidizing medium and carbon dioxide used for pressurize the feed hopper, the reactor effluent gases, in addition to the gases formed in the pyrolysis, contained these supplied gases. The composition of the nitrogen in the reactor off gases varied from 48 to 53 mole percent. However, to study the effect of particle size and temperature on the pyrolysis, the composition of the product gases were calculated on a nitrogen and supplied carbon dioxide free basis. Tables 5 to 7 show the composition of net produced gas at different temperatures for three mesh sizes. The tables indicate that for every mesh size studied besides methane, hydrogen, carbon monoxide, carbon dioxide some other gases were also produced. These gases were determine

TABLE 5 : COMPOSITION OF NET PRODUCED GAS BY PYROLYSIS OF BOVINE WASTE FRACTION (-30+44) MESH SIZE

Basis : 100 gm. moles of net produced gas

COMPONENT	TEMPERATURE °C				
	600	650	700	750	800
	gm.mole	gm.mole	gm.mole	gm.mole	gm.mole
CH_4	14.43	13.85	11.44	9.39	9.36
H_2	16.56	17.67	23.35	26.5	26.64
CO	35.19	37.7	42.51	44.34	46.28
CO_2	27.5	24.57	17.91	15.58	15.44
Other Gases	6.42	6.21	4.79	4.18	2.28
TOTAL	100	100	100	100	100

TABLE 6 : COMPOSITION OF NET PRODUCT GASES BY PYROLYSIS OF BOVINE WASTE FRACTION (-44+72) MESH SIZE

Basis : 100 gm. moles of Net Produced Gas

COMPONENTS	TEMPERATURE °C				
	600	650	700	750	800
	gm.mole	gm.mole	gm.mole	gm.mole	gm.mole
CH_4	16.13	15.10	12.12	10.41	10.04
H_2	19.03	21.26	25.10	26.92	27.48
CO	30.81	35.78	37.88	42.31	43.16
CO_2	30.52	20.27	19.05	15.29	14.32
Other Gases	3.51	7.59	5.85	5.10	4.99
TOTAL	100	100	100	100	100

TABLE 7 : COMPOSITION OF NET PRODUCED GASES BY PYROLYSIS OF BOVINE WASTE FRACTION (-72+100) MESH SIZE

Basis : 100 gm. mole of Net Produced Gas

COMPONENTS	TEMPERATURE°C				
	600	650	700	750	800
	gm.mole	gm.mole	gm. mole	gm.mole	gm. mole
CH_4	16.44	15.79	12.58	10.89	10.25
H_2	21.14	24.75	26.54	28.1	28.28
CO	22.34	27.48	25.93	38.56	40.77
CO_2	34.51	27.47	21.51	19.83	18.64
Other Gases	5.77	4.51	3.44	2.62	2.06
TOTAL	100	100	.00	100	100

by the nitrogen mass balance and off gas analysis for methane, hydrogen, carbon monoxide and carbon dioxide. The amount of unaccounted gases decreases with an increase of temperature for every particle size. Figures 6 to 9 show the effect of temperature and particle size on composition of methane, hydrogen, carbon monoxide and carbon dioxide respectively.

Figure 6 shows the variation of mole percent of methane in produce gas with temperature. For all particle sizes studied, with an increase in temperature, mole percent of methane in product gas decreased. The drop in molar percentage of methane with temperature is very high in the temperature range of 650-750°C. This is due to reaction No. (iii), rate of which is significant at 650°C, and it is nearly complete at temperature around 750°C. Therefore increase in temperature beyond 750°C brings about no change in molar percentage of methane in product gases. Habibulla[20] pyrolysed manure samples of feed in a fixed bed reactor at temperatures ranging from 400-650°C. He found that concentration of methane first increased with temperature, attained a maximum at around 550°C then started decreasing with increasing the temperature.

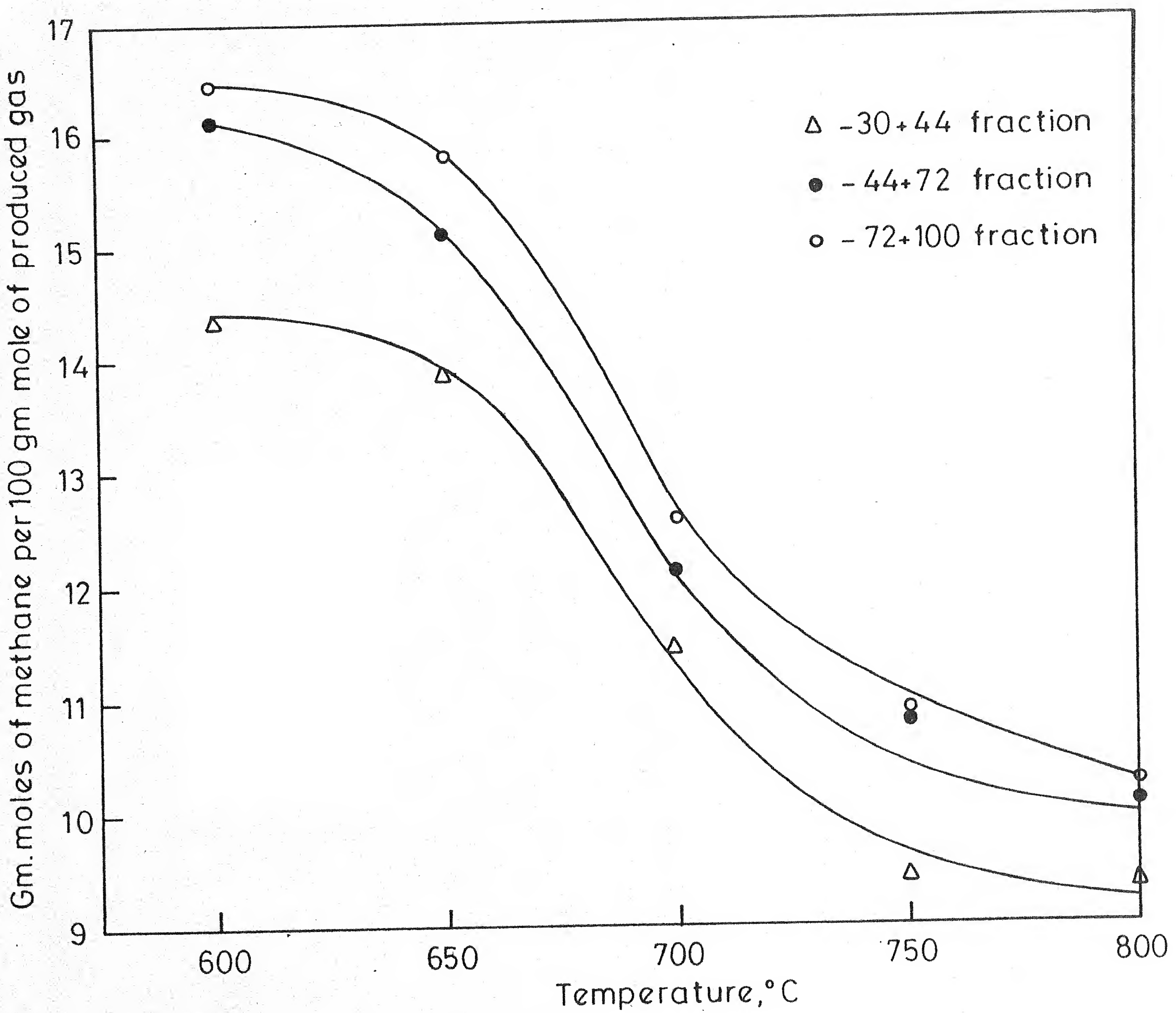


Fig. 6 : Effect of temperature and particle size on mole percent of methane.

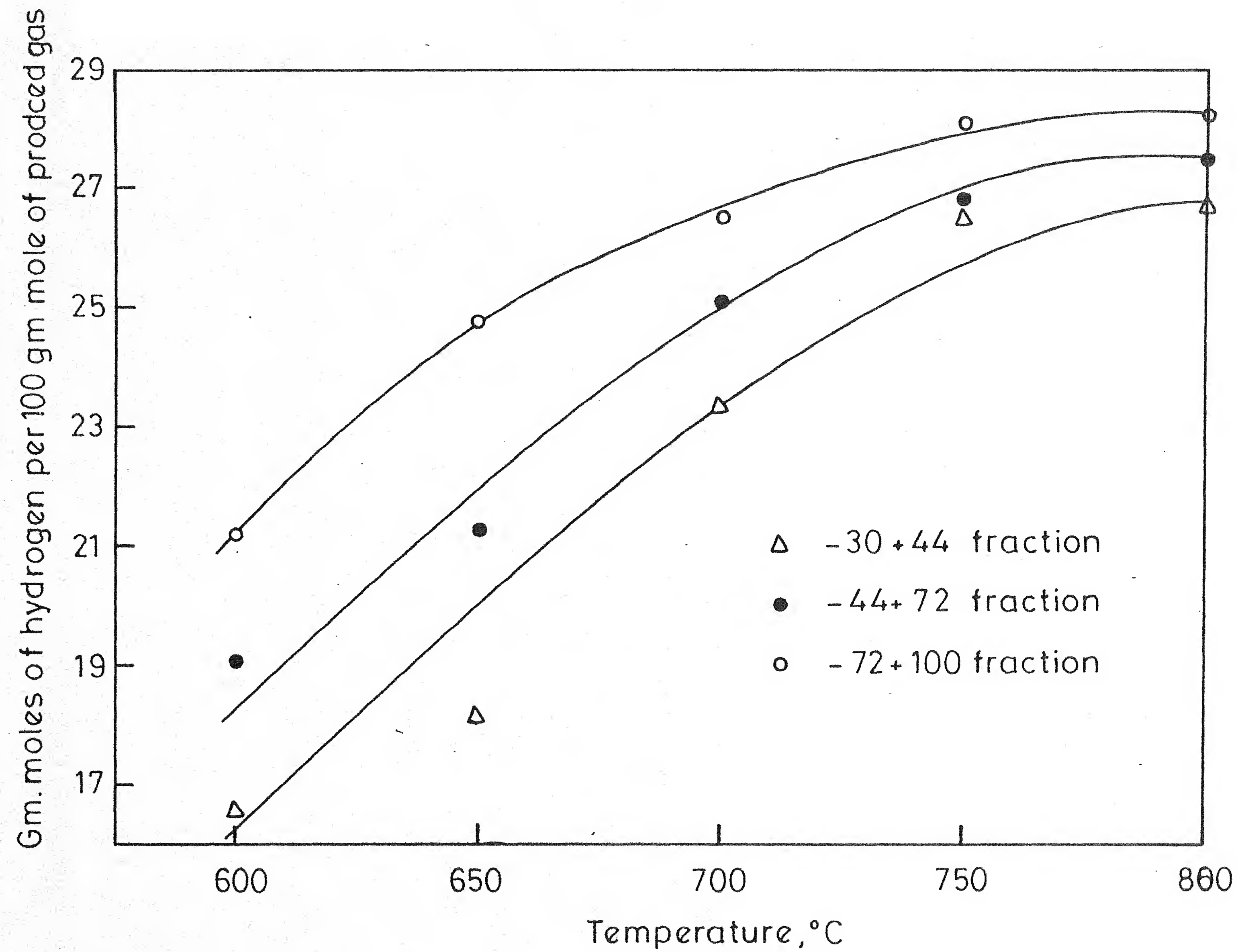


Fig. 7 : Effect of temperature and particle size on mole percent of hydrogen.

Hoffman[16] too observed the maximum molar percentage of methane at around 650°C for pyrolysis of municipal refus In our study no maxima were observed, howevever it is expected that maxima would be obtained at temperature lower than 600°C. The trend agreed well with the results presented by Hoffman[16] for temperatures higher than 650

Fig. 6 also shows that at the same temperature molar percentage of methane was higher for smaller particl than that for larger ones at the same temperatures. The net result of decrease in particle size should have the effect of increasing the effective temperatures as discuss earlier and it would be expected that for the same temperature, the CH_4 content should decrease with decreasing particle size. However, the feed characterization in Table 1 shows that hydrogen to carbon ratio is 1.5 times more for -72+100 mesh size than that for -30+44 mesh size. Therefore in pyrolysis, formation of methane and hydro is favoured for smaller particle size.

Fig. 7 shows that hydrogen mole percent increased with an increase in temperature for all particle sizes studied. For example for -30 + 44 fraction, the hydrogen mole percent increased from 15.6 at 600°C to 26.6 at 800°C.

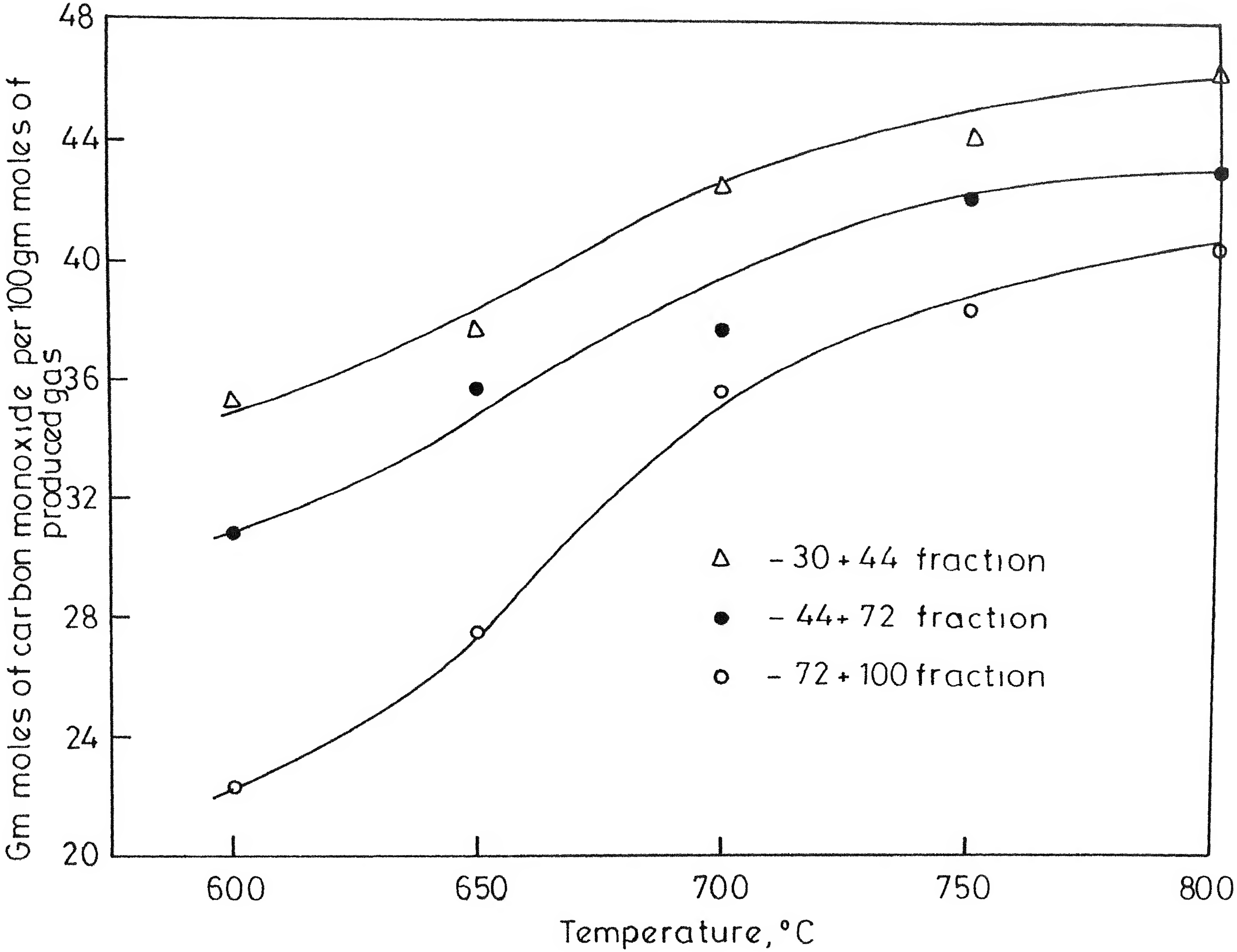


Fig 8 Effect of temperature and particle size on mole percent of carbon monoxide

Reactions (i), (iii) & (iv) are responsible for this increase. These results are in agreement with those of Hoffman[16] for municipal solid waste refuse. He found that hydrogen concentration increased from 18% at 650°C to 28% at 850°C.

For the same temperature, decrease in the particle size caused an increase in hydrogen mole percent. For example at 600°C, hydrogen mole percent increased from 16.6 percent for -30+44 mesh size to 21.2 percent for -72+100 mesh size feed. At the corresponding temperature Habibulla[20] observed that hydrogen mole percent increased from 28.2 percent for -13+30 mesh size manure feed to 36.1 for -72+100 mesh size manure feed. The hydrogen content of his feed was 6.0%. The lower hydrogen yields found in this study were probably due to the lower hydrogen content of the waste feed.

Fig. 8 shows that for all particle size fractions studied, mole percent of carbon monoxide in product gases increased with an increase in temperature. Reaction (i), (ii) & (iii) increase the concentration of carbon monoxide while reaction (iv) decreases the carbon monoxide concentration.

However, at high temperatures reaction (iv) is very fast and can be considered to be at equilibrium[22]. Moreover, reaction (iv) is slightly exothermic and increasing the temperature will favour the concentration of carbon monoxide. Increasing the temperature increases reactions (i) to (iii) and therefore carbon monoxide concentration increases with temperature. Since at higher temperatures most of the carbon has reacted, the effect of temperature on carbon monoxide concentration is not appreciable. It explains why carbon monoxide increased slowly at higher temperature than at lower temperatures.

For the same temperature mole percentage of carbon monoxide in product is more for larger particles size than that for smaller particle size. It can be explained in this way. If it is assumed that components present in feed are carbon, hydrogen, nitrogen, moisture ash and rest is oxygen, from Table 1 it is found that carbon to oxygen ratio is more for larger particle size fraction, Thus the formation of carbon monoxide relative to carbon dioxide is favoured for larger particles. Therefore the mole percent of carbon monoxide in the product gases increases with the increase in particle size.

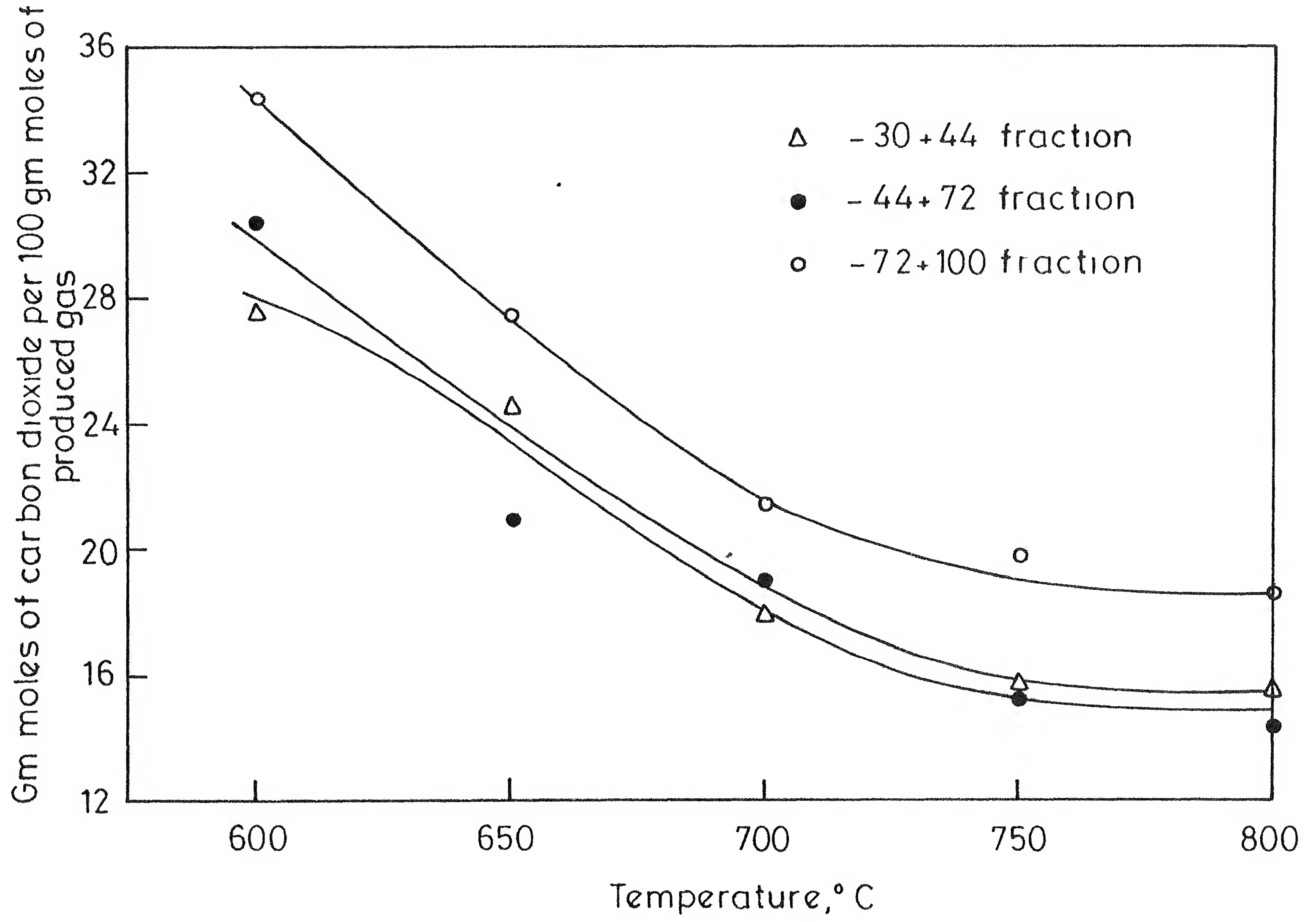


Fig. 9 Effect of temperature and particle size on mole percent of carbon dioxide

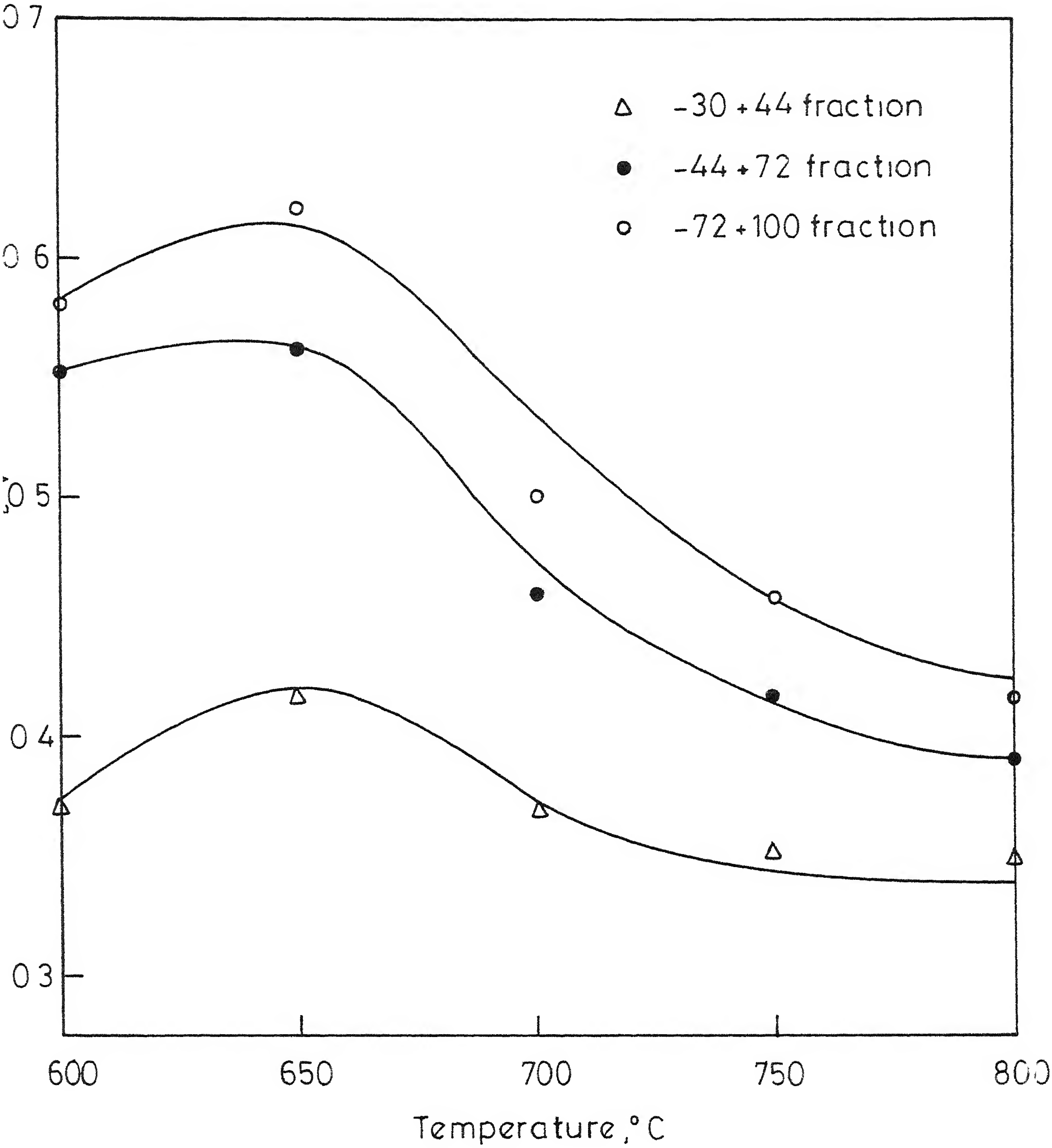


Fig 10 Effect of temperature and particle size on yield of methane

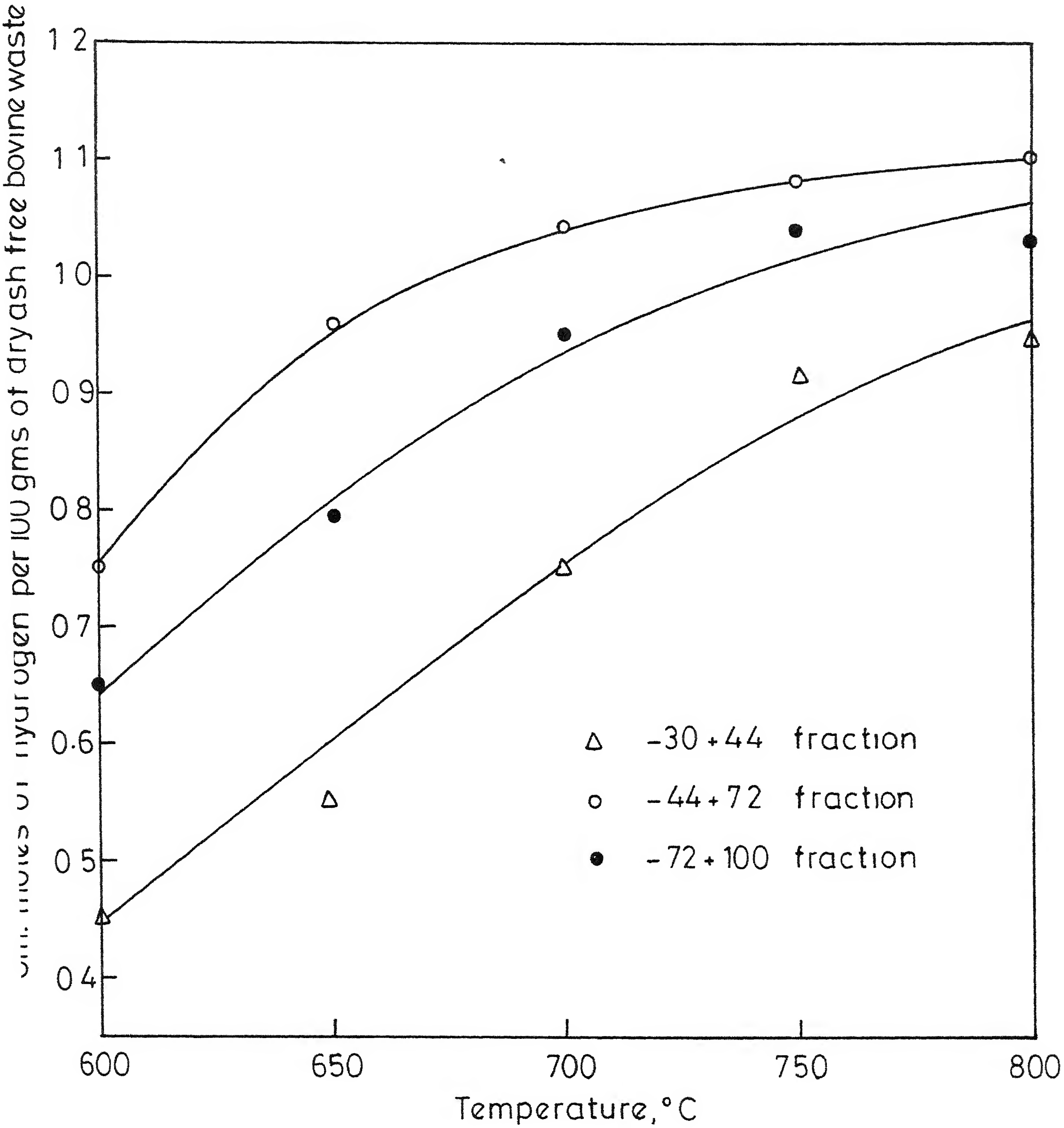


Fig 11 Effect of temperature and particle size on yield of hydrogen

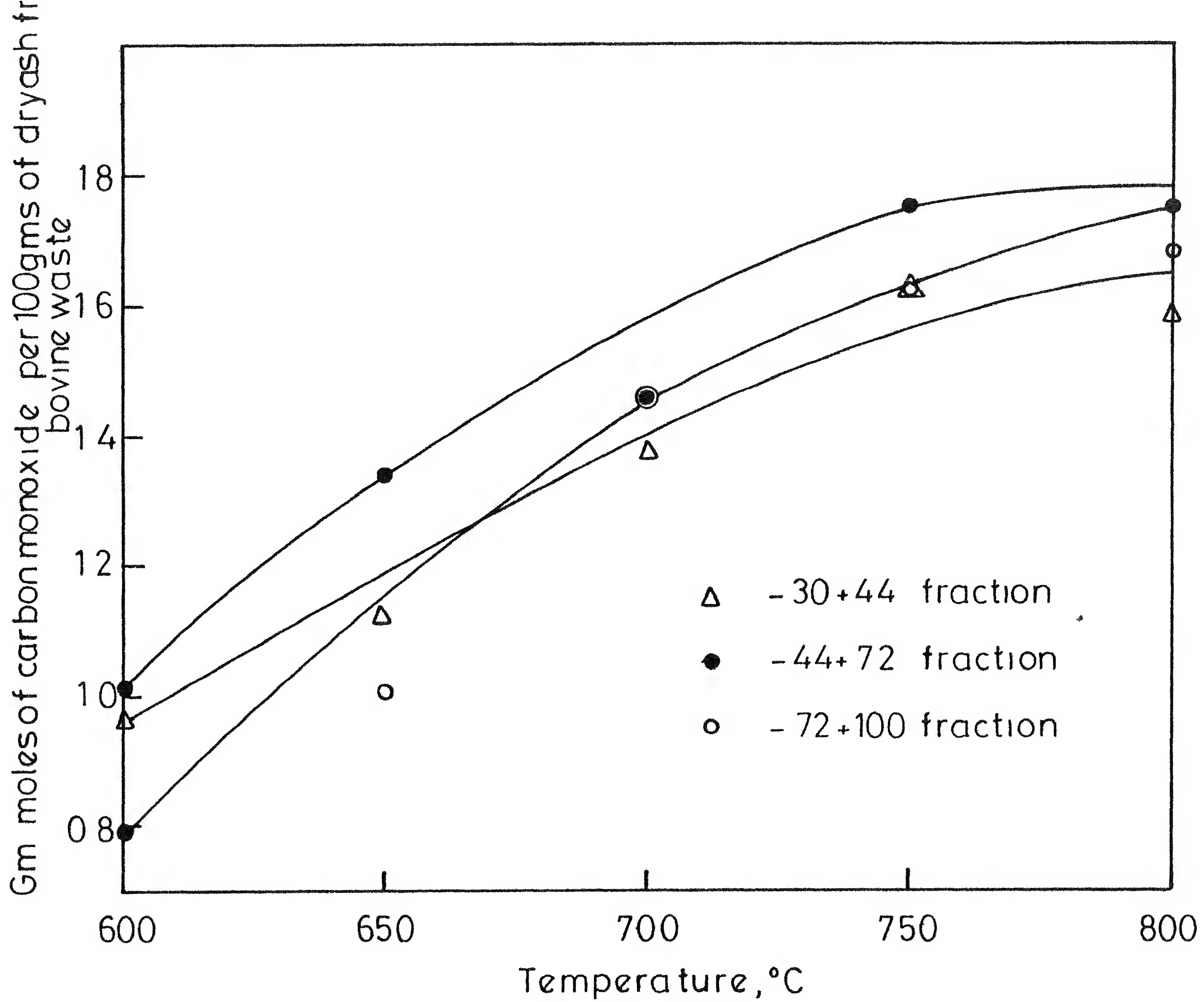


Fig 12 Effect of temperature and particle size on yield of carbon monoxide

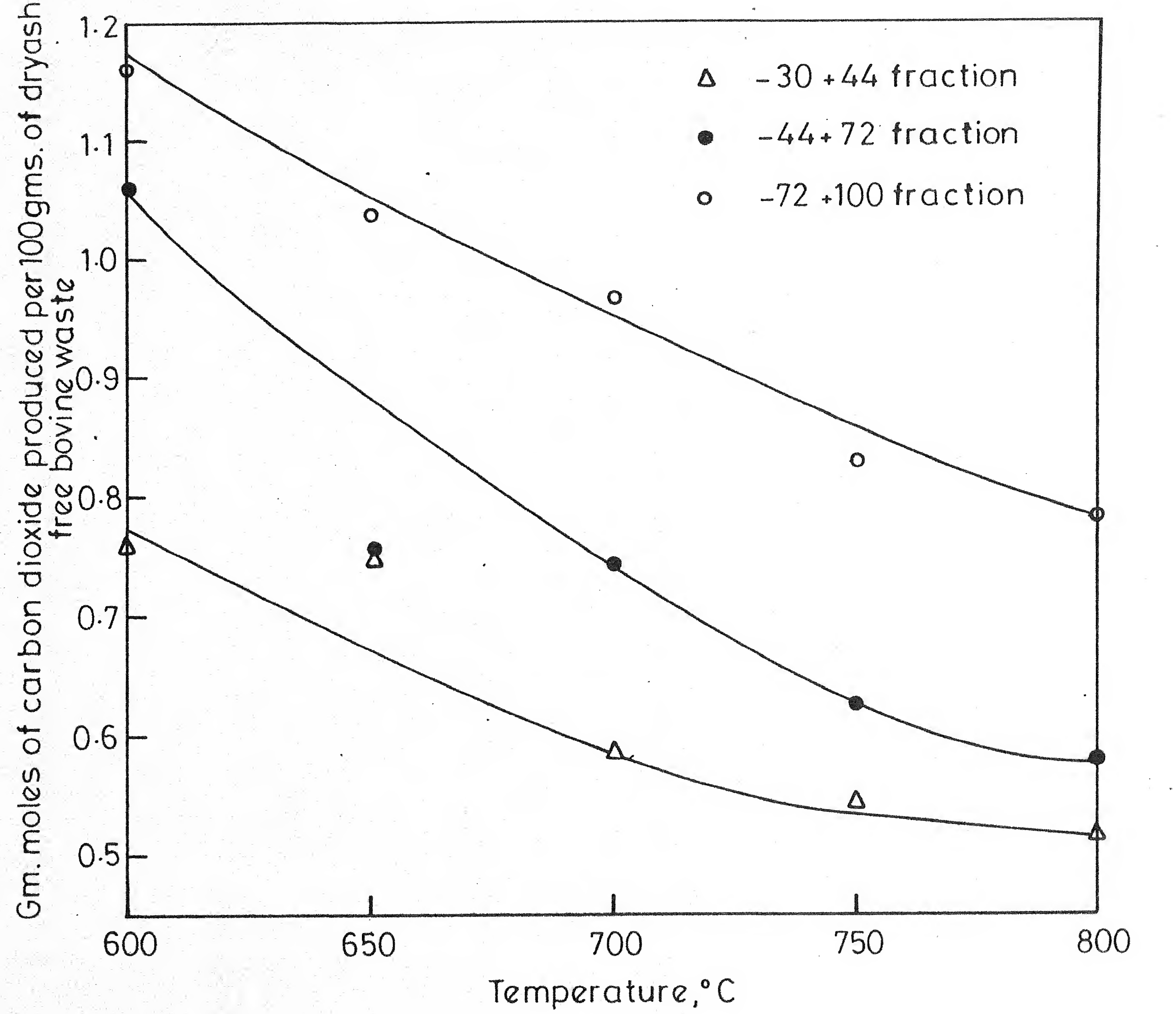


Fig. 13 : Effect of temperature and particle size on yield of carbon dioxide.

Fig. 9 shows that with an increase of temperature, carbon dioxide decreases for all particle sizes. The carbon dioxide formed reacts with the carbon present in the feed to form carbon monoxide, thus the composition of carbon dioxide decreases with temperature. At higher temperatures, the carbon dioxide concentration levels off. This is because most of the organic compounds of the feed have reacted.

The effect of particle size on carbon dioxide concentration can again be explained on the basis of relative oxygen content of the feed as discussed earlier for explaining the trend of carbon monoxide concentration with particle size.

4.4 Effect of Particle Size and Temperature on Yields of Various Gases Components

For practical purposes one would be more interested to know the total moles of components rather than their mole percent in product gases. Therefore figures 10 to 13 are presented to show the effect of temperature and particle size on molar yields of individual gaseous components per 100 gram dry ash free bovine waste feed.

Fig. 10 shows that yields of methane are maximum at temperatures around 650°C for all particle sizes. This is due to the combined effect of the increase in total gas yield and a decrease in the molar percentage with increasing temperature.

As shown in Figures 11 and 12 the yields of hydrogen and carbon monoxide increases with temperature for all the three particle sizes. This is because for the two components the mole percent and the total gas yield increases with temperature. As discussed earlier, the mole percent of carbon dioxide decrease while the total gas yield increases with temperature and the net effect on the yield of carbon dioxide is a slight decrease with temperature increase and particle size decrease.

4.5 Heating Values of Products

The heating values of the product gases and chars obtained by pyrolysis of the different mesh fractions at different temperatures are shown in Table 8. It was found that with an increase in the pyrolysis temperature and decrease in the particle size, the ash content of the product char increased and its heating value decreased.

TABLE 8 : HEATING VALUES OF THE PRODUCT GAS AND CHAR

Sl. No.	Mesh Size	Temp °C	Heating value of the Char, Cal. per gm.	Heating value of product gases, KCal per m^3 at STP
1	-30+44	600	2480	2650
2		650	2450	2830
3		700	2420	2890
4		750	2380	2960
5		800	2390	2890
6	-44+72	600	2360	2810
7		650	2340	2950
8		700	2300	2810
9		750	2210	2770
10		800	2100	2710
11	-72+100	600	2300	2740
12		650	2105	2910
13		700	1920	2880
14		750	1540	2840
15		800	1380	2840

TABLE 9 : ENERGY BALANCE FOR PYROLYSIS OF BOVINE WASTE FRACTION (-30+44)

Basis : 100 gram dry ash free feed

Temperature °C	600 KCal	650 KCal	700 KCal	750 KCal	800 KCal
<u>Input</u>					
Bovine waste (-30+44)	458	458	458	458	458
<u>Output</u>					
CH_4	78.74	88.52	78.74	70.22	70.22
H_2	31.42	36.89	51.24	62.85	62.85
CO	64.93	75.76	92.67	109.58	106.87
CO_2	0	0	0	0	0
Other Gases	0	0	0	0	0
Total Gases	175.09	201 17	222.65	242.65	239.94
Char	104.46	99.03	92.69	86.85	87.45
Total output	280.6	300.2	315.4	329.5	329.3
Recovery (%)	61.3	65.5	66.6	68.8	72

TABLE 10 : ENERGY BALANCE FOR PYROLYSIS OF BOVINE WASTE FRACTION (-44+72)

Basis : 100 gram dry ash free feed

TEMPERATURE°C	600 KCal	650 KCal	700 KCal	750 KCal	800 KCal
<u>Input</u>					
Bovine Waste (-44+72)	453	453	453	453	453
<u>Output</u>					
CH_4	117.68	119.17	97.89	89.38	89.38
H_2	44.41	53.97	64.90	73.79	71.05
CO	71.70	90.64	98.75	118.37	113.63
CO_2	0	0	0	0	0
Other Gases	0	0	0	0	0
Total Gases	233.79	263.78	261.54	274.54	274.06
Char	112.9	105.1	112.93	97.7	80.93
Total Output	346.69	368.9	374.5	372.2	355
Recovery (%)	76.5	81.4	82.6	84.6	78.3

TABLE 11 : ENERGY BALANCE FOR PYROLYSIS OF BOVINE WASTE FRACTION (-72+100)

Basis : 100 gram dry ash free bovine waste

TEMPERATURE °C	600 KCal	650 KCal	700 KCal	750 KCal	800 KCal
<u>Input</u>					
Bovine waste (-72+100)	461	461	461	461	461
<u>Output</u>					
CH_4	123.4	131.9	106.4	97.89	89.38
H_2	51.24	65.59	73.78	79.25	81.98
CO	53.44	70.35	98.75	109.57	180.37
CO_2	0	0	0	0	0
Other Gases	0	0	0	0	0
Total Gases	228.08	267.84	278.93	286.71	289.73
Char	125.37	111.0	95.63	71.61	62.2
Total Output	353.45	378.84	374.6	358.3	352.0
Recovery (%)	76.5	82.17	81.3	77.8	76.2

The heating values varied from 1380 KCal per kg. for the -72+100 mesh particles at temperature 800°C to 2480 KCal per kg. for -30+44 at 600°C.

This is because at higher temperatures, a higher percentage of the carbon is converted to gaseous product.

Little variation in heating values of the product gas (from 2650 KCal/kg. for -30+44 mesh size, at 600°C to 2950 KCal/kg. for -44+72 mesh size at 650°C) occurred. The heating values of the product gases were maximum, at 650°C for -44+72 & -72+100 mesh size, while at 700°C for -30+44 mesh fraction. However as shown in Tables 9 to 11 the heating values of the total gases produced per 100 gram dry ash free feed was maximum at 750°C for the three fractions. The maximum value increased from 242.65 KCal/per 100 gm. dry ash free feed for -30+44 mesh size to 288 KCal per 100 gm. feed for -72+100 mesh size. The energy balance for pyrolysis of fractions -30+44, -44+72, & -72+100 is also shown in Tables 9, to 11.

These tables show that the total heat recovery varied from 61 to 85 percent. The poor heat recoveries were because of two reasons. Firstly the heating values of

the unidentified gases, most of which according to Hoffman and others[16] are ethylene and ethane, having a heating value of 373 KCal per gm. mole were neglected. Secondly the tarry liquids which adhered to the wall of the condensor and cyclone were not taken into account. According to Mc Farland[21], these have a heating value of 11.5 KCal/gm. and would therefore appreciably effect the heat recovery even if present in small amounts.

CHAPTER 5

CONCLUSIONS

A lab scale set up was successfully developed for pyrolysis of solid bovine waste in a fluidized bed reactor and from the experiments carried out on pyrolysis, the following conclusions can be made :

1. For the same particle size, the yield of gases produced increased as the temperature was increased. However, in the range of particle size studied the gas production increased by 8.5% as the temperature was increased from 600 to 800 °C.

2. For the same temperature, weight of gas produced per unit weight of ash free solid decreased as the particle size of the feed was increased.

3. For the same particle size, molar yields per unit weight of feed, showed a maximum at 650 °C for methane, while for hydrogen and carbon monoxide increased continuousl with increasing temperature.

4. For the same temperature yields of hydrogen and methane decreased as the particle size was increased.

5. The heating value of the product gases varied with temperature and particle size and were highest for -30+44 mesh size feed and 650°C. The highest heating values of the product gas for -30+44, -44+72 and -72+100 were 2960, 2950 and 2910 KCals. per cubic meter respectively.

6. For any particle size, the heating value of the char decreased with increasing temperature and at the same temperature heating value decreased as the particle size decreased.

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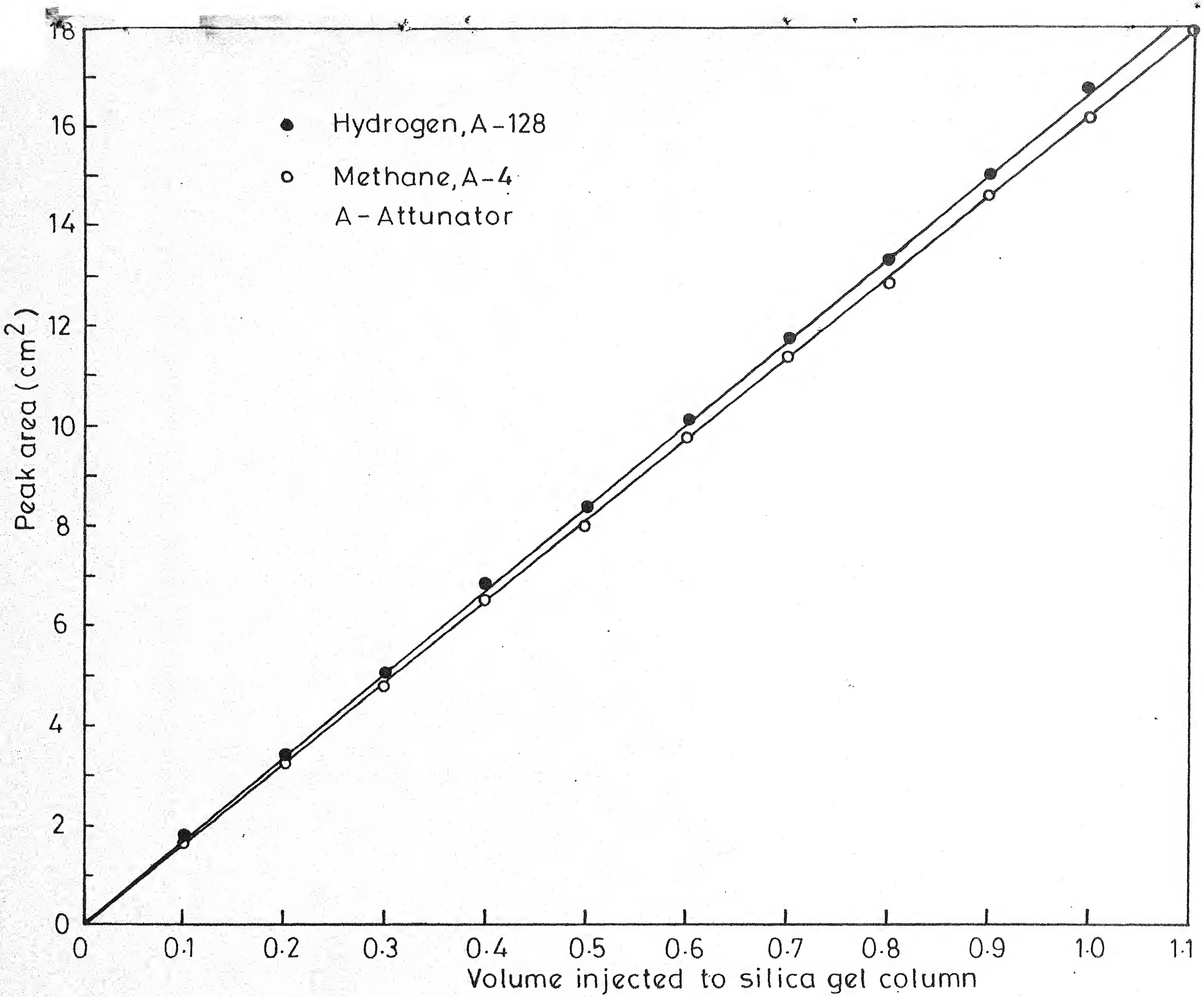

Fig. 14 : Calibration curves for gases.

APPENDIX 3

STANDARD HEATS OF COMBUSTION (24)

Reference conditions : 25 °C, 1 atm pressure,

H_c^o = Standard heat of combustion

g = Gaseous

Compound	Formula	$- H_c^o$, KCal/gmole
Carbonmonoxide	$CO(g)$	67.6361
Hydrogen	$H_2(g)$	68.3174
Methane	$CH_4(g)$	212.798

APPENDIX 4

DENSITIES OF GASES AT STANDARD CONDITIONS(23)

(0 °C, 1 atm)

Compound	Formula	Mol.Wt.	Density G/lit.	
Carbonmonoxide	$CO(g)$	28.0	1.2501	0.
Carbon dioxide	$CO_2(g)$	44.0	1.9768	
Hydrogen	$H_2(g)$	2.016	0.0898	
Methane	$CH_4(g)$	16.03	0.7167	

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